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We discuss the case of the Cu/Au(111) UPD, which is treated as a sequence of three uncoupled phase transitions. Phenomenological rate constants are derived fitting the theory to the experiments of Kolb et al.

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KINETIC THEORY FOR ELECTRODIC PHASE TRANSITIONS: THE VOLTAMMOGRAM

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Kinetic Theory of Phase Transitions at Electrode Surfaces: The Voltammogram

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Abstract

In recent papers we investigated the equilibrium statistical mechanics of phase transitions at electrode interfaces. We derived the adsorption isotherm $\theta = \mathcal{A}(\hat{z}, \hat{u}) / \{1 + \mathcal{A}(\hat{z}, \hat{u})\}$ in which both \hat{z}, \hat{u} are functions of molecular parameters and the applied potential, which satisfies correct scaling to any desired accuracy. Implicit in our model is the approximation that each transition is treated as a single adsorbate onto a sublattice of the available adsorption sites. This form can be extended to include reaction and diffusion kinetics. We discuss the cases with diffusion (small bulk concentration) and without diffusion (large bulk concentration). For the latter our model is solved mathematically, and we get explicit formulas for the shifts of the peaks, in terms of the overall kinetic reaction constants. Asymptotic formulae for slow scanning rates are given.

We discuss the case of the Cu/Au(111) UPD, which is treated as a sequence of three uncoupled phase transitions. Phenomenological rate constants are derived fitting the theory to the experiments of Kolb et al.

1 INTRODUCTION

In previous work we have proposed the sticky site model (SSM) for the chemisorption of adsorbates from fluids onto crystal surfaces [1, 2]. The crystal surface is represented by an array of sticky point adsorption sites. This permits the formal decoupling of the statistical mechanics into the 1-dimensional problem of the smooth electrode near an electrolyte, (the classic double layer problem), and the 2-dimensional lattice gas of the adsorption onto the array of sticky sites. In this model the binding process of individual atoms is coupled to the cooperative effects that take place at the surface through mean field parameters, and the adsorption process is treated by studying the two dimensional lattice gas of the adsorbates, with two parameters obtained from the double layer problem:

- The lattice gas fugacity

$$\hat{z}_i = \lambda_i \rho_i(0, \psi) \quad (1)$$

where λ_i is the binding probability of the adsorbate to the individual site and $\rho_i(0, \psi)$ is the contact density of the ion i for the smooth electrode surface. [12, 13, 14].

- The probability g_2 of two adsorbate atoms to be in two neighboring adsorption sites. In our theory it turns out to be the pair correlation function of the adsorbates in contact with the smooth electrode wall [1]

$$g_2 = g_2^0(r_{ij}). \quad (2)$$

These two parameters determine the equilibrium phase behavior of the adsorbate. Our model gives exact conditions for g_2 for the occurrence of phase transitions, which were discussed in our previous work [1, 2].

In the present work we extend the equilibrium (zero scanning rate) theory to include the dynamic regime of non-zero scanning rates. We do that by using a simple mean field argument. In section 2 we describe the basic theory for the case without mass transport, which is explicitly solved. In section 3 we include diffusion and mass transport. In section 4 we apply our theory to the underpotential deposition of Cu onto Au(111), and we give a

short discussion of our results.

2 KINETIC MODEL, NO DIFFUSION

There is a very extensive literature on the voltammograms for the electrodeposition of metals, starting with the early work of Koryta [3], Delahay [4], Brdicka [5], Guidelli [6], Laviron [7], Lorenz [8], Reinmuth [9], Sadkowski [10] and Lantelme [11]. However these models do not consider the case of adsorption onto a lattice with cooperative effects, such as phase transitions. In our statistical mechanics treatment of phase transitions in the ad-layers [2, 12, 13, 14] the adsorption isotherm is written in the form of a Padé approximant, which represents to any required precision the exact coexistence line and universal critical behaviour. This form of the isotherm lends itself to a simple way to include kinetic effects, which in the limit of very slow scanning rates gives back the required equilibrium phase behaviour.

The details of the kinetics of the formation of the monolayer adsorbates has been discussed in the past [15, 16, 17]. We believe that the discussion of nucleation processes can be included in our more general, linear response type theory, by specific choices of the time dependence of the kinetic constants K_a and K_d (see below).

In our treatment we restrict ourselves to single species adsorption onto a lattice. Multiple species adsorption [18] will not be discussed here as such. However, in the example of the underpotential deposition of Cu onto Au(111) in the presence of sulphuric acid as discussed below, multiple adsorption is treated as a sequence of single species adsorption processes onto sublattices of the substrate.

A kinetic equation for the fraction of occupied sites θ_i can be obtained from a simple probabilistic argument. The probability of a site to be occupied by i is proportional to the density of i at the electrode surface and the number of free sites.

$$\rho_i(0, \psi)(1 - \theta_i) \quad (3)$$

The probability of an ion that is adsorbed to be dissolved is proportional to θ_i . Therefore, the rate of change is

$$\frac{\partial \theta_i}{\partial t} = K_a \rho_i(0, \psi)(1 - \theta_i) - K_d \theta_i \quad (4)$$

The two reaction rate constants K_a and K_d must satisfy at equilibrium the relation

$$\theta = \mathcal{A}(\hat{z}, \hat{u}) / \{1 + \mathcal{A}(\hat{z}, \hat{u})\} \quad (5)$$

and therefore

$$\mathcal{A} = \mathcal{A}(\hat{z}, \hat{u}) = \frac{K_a \rho_i(0, \psi)}{K_d} \quad (6)$$

Here \mathcal{A} is a polynomial defined in our previous work [1, 2]. The coefficients of this polynomial are obtained from exact high and low fugacity expansions. The variables are the individual species fugacity \hat{z} , and the lateral interaction parameter g_2 . However, it is more convenient to use the variable

$$\hat{u} = \hat{z}[g_2]^{q_L/2}, \quad (7)$$

where q_L is the number of neighbors of the lattice (6 for the triangular (center filled regular hexagons) lattice and 3 for the honeycomb (empty center hexagons)). In our model, and because of the Yang-Lee theorem [2] the coexistence line is given by

$$\hat{u} = 1 \quad (8)$$

so that for the discussion of the phase transitions we need to consider only the range $\hat{u} \simeq 1$.

The equilibrium requirement is satisfied for any K_d with an arbitrary time or voltage dependence. A form consistent with Tafel's equation[19] is

$$K_d = K_0 e^{\alpha_T \psi}, \quad (9)$$

where α_T is the so called Tafel parameter. Eq.(4) is conveniently written in the form

$$\frac{\partial \theta_i}{\partial t} = -\theta_i K_{ad} + K_a \rho_i(0, \psi), \quad (10)$$

where we have defined

$$K_{ad} = K_a \rho_i(0, \psi) + K_d. \quad (11)$$

Equation (10) is a first order differential equation that has an explicit solution in terms of the time dependent coefficients K_{ad} , $K_a\rho_i(0, \psi)$. The time dependence of these constants is completely arbitrary. No assumptions or models are required by our mathematical treatment. If the scanning of the potential is linear, as in the voltammogram, the potential and the time are equivalent variables. But for a different experiment, such as for example chronocoulometry, this is not necessarily so. We have

$$\theta_i = e^{-\int_0^t dt_1 \{K_{ad}\}} \theta_0 + \int_0^t dt_1 K_a \rho_i(0, \psi) e^{\int_{t_1}^t dt_2 \{K_{ad}\}} \quad (12)$$

We define the fraction of occupied sites for an infinitely slow scanning rate

$$\theta_i^\infty(t) = \frac{K_a \rho_i(0, \psi)}{K_{ad}} = \frac{\mathcal{A}}{1 + \mathcal{A}}, \quad (13)$$

so that Equation (10) can be written in the simpler form

$$\frac{\partial \theta_i}{\partial t} = -[\theta_i - \theta_i^\infty] K_{ad}, \quad (14)$$

which in turn can be written as

$$\frac{\partial \Delta \theta_i}{\partial t} = -\Delta \theta_i K_{ad} - \frac{\partial \theta_i^\infty}{\partial t}, \quad (15)$$

with

$$\Delta \theta_i = [\theta_i - \theta_i^\infty], \quad (16)$$

The solution of Eq.(15) is

$$\Delta \theta_i(t) = \Delta \theta_i(0) e^{-\int_0^t dt_1 \{K_{ad}(t_1)\}} - \int_0^t dt_1 \frac{\partial \theta_i^\infty(t_1)}{\partial t_1} e^{-\int_{t_1}^t dt_2 \{K_{ad}(t_2)\}}, \quad (17)$$

We consider here the case in which we have a linear potential sweep

$$\psi = \psi_{in} + vt \quad (18)$$

where ψ_{in} is the initial value of the potential, and v is the scanning rate. Then, we can use ψ as our new variable. Iteration of Eq(17) yields the series in v , for low scanning rates and with the assumption $\Delta \theta_i(0) = 0$

$$\theta_i(\psi) = \theta_i^\infty(\psi) - \frac{v}{K_{ad}(\psi)} \frac{\partial \theta_i^\infty(\psi)}{\partial \psi} + \frac{v^2}{K_{ad}(\psi)} \frac{\partial}{\partial \psi} \left[\frac{1}{K_{ad}(\psi)} \frac{\partial \theta_i^\infty(\psi)}{\partial \psi} \right] - \dots \quad (19)$$

This equation should be useful in calculating the overall kinetic constants K_{ad} from the shifts in the voltammogram.

A simple useful formula that can be obtained from this equation is that for small scanning rates v the zero scanning rate limit is given by

$$\theta_i^\infty(\psi) = (1/2) [\theta_i^{oxid}(\psi) + \theta_i^{red}(\psi)], \quad (20)$$

where $\theta_i^{oxid}(\psi)$ is the isotherm for oxidation scan and $\theta_i^{red}(\psi)$ for the reduction scan. A corollary to this relation is the convenient formula

$$\theta_{spike}^{v=0} = (1/2) [\theta_{spike}^{strip} + \theta_{spike}^{deposit}]. \quad (21)$$

An illustration of these equations for this case without diffusion is shown in Figure 1. Since we are interested in sharp transitions we lose essentially no accuracy in writing (see ref. [20] for a detailed discussion of this point)

$$\mathcal{A} \simeq a\hat{z}^n \quad (22)$$

This form implies that the fraction of occupied sites is a broadened step or Heaviside function. The width of the corresponding voltammogram spike is inversely proportional to n .¹ The physical meaning of the parameter n is connected with the intrinsic width of the transitions due to defects, impurities, domain size, and also to the instrumental width of the experiment. In Figure 1 the shifts for different values of n are shown. For any value of the width the limiting slope is the same, and therefore, the value of the kinetic constant K_{ad} can be deduced from experiments done at different scanning rates v using equation (19).

¹More precisely

$$\left[\frac{n+1}{n-1} \right]^{\frac{n-1}{n}} \frac{4n}{(n+1)^2}$$

for $n > 1$. For large n this is approximately $\simeq 4/n$

3 CASE WITH DIFFUSION

We consider now the diffusion process in the following simplified way: We will assume that since the scanning rate is low, the system is always close to equilibrium. The important parameter is \hat{u} Eq.(7). We recall also that

$$\hat{z}_i = \lambda_i \rho_i(0, \psi) \quad (23)$$

Furthermore, the lateral interaction parameter g_2

$$g_2 = g_2^0(\mathbf{R}_i, \mathbf{R}_j) \quad [i, j = \text{nearest lattice neighbors}], \quad (24)$$

where g_2^0 is the pair correlation of the adsorbates sitting in neighboring adsorption sites but for the undecorated, smooth electrode surface. If the parameter \hat{u} is less than unity then we are in the 1 phase region. If it is larger than 1, then we are in the two phase region. The coexistence curve is obtained setting $\hat{u} = 1$ in Eq.(7).

Our basic assumption is that we now introduce as our new variables

$$z_i(t) = \hat{z}_i \rho_i(0, t) / \rho_i \quad (25)$$

$$u_i(t) = \hat{u}_i \rho_i(0, t) / \rho_i \quad (26)$$

where ρ_i is the bulk concentration of i . We get the ratio

$$\gamma_i(t) = \rho_i(0, t) / \rho_i \quad (27)$$

from free diffusion theory, which is completely consistent with the treatment usually given in the textbooks of electrochemistry[19].

The current density is

$$j_i = i_i / A \quad (28)$$

where i_i is the current intensity and A is the area of the electrode, obeys the continuity equation

$$\frac{\partial \rho_i(0, t)}{\partial t} = - \frac{\partial j_i}{\partial z} \quad (29)$$

and in principle the linear relaxation yields for the current density

$$j_i = -D_i \frac{\partial \rho_i(0, t)}{\partial z} + \kappa_i \rho_i(0, t) E(0) \quad (30)$$

where D_i is the diffusion constant of i , $\rho_i(0, t)$ is the contact density at time t , κ_i is the transport coefficient and $E(0)$ is the electric field at $z = 0$. Following the common practice in the literature [19, 21], we ignore field effects in the diffusion. This however means that the diffusion coefficient D_i is an effective diffusion parameter which includes the barrier effects of the double layer, which is different for anions and cations.

The diffusion equation is

$$\frac{\partial \rho_i(z, t)}{\partial t} = D_i \frac{\partial^2 \rho_i(z, t)}{\partial z^2} \quad (31)$$

with the boundary conditions

$$t = 0 \quad \rho_i(z, 0) = \rho_i$$

which implies that we assume that initially the system is in equilibrium, and that the initial density profile is uniform. More precisely

$$t > 0 \quad \rho_i(\infty, t) = \rho_i \quad (32)$$

where the bulk concentration is ρ_i .

When

$$t > 0 \quad z = 0$$

we assume that all the ions that have arrived by diffusion to the electrode either react or are diffused back into the solution. Mass conservation Eq.(29) yields at the electrode surface

$$j_i = -D_i \frac{\partial \rho_i(0, t)}{\partial z} = \frac{\partial \Gamma_i}{\partial t} = m \frac{\partial \theta_i}{\partial t} \quad (33)$$

where the surface concentration Γ_i is given in terms of the fraction of occupied sites θ_i and the number of sites M per unit area A :

$$m = M/A$$

$$\Gamma_i = m \theta_i \quad (34)$$

We solve the diffusion equation (31) by Laplace transformation:

Define

$$\tilde{\rho}_i(z, s) = \int_0^\infty dt e^{-st} \rho_i(z, t) \quad (35)$$

then

$$\frac{d\tilde{\rho}_i(z, s)}{ds} = s\tilde{\rho}_i(z, s) - \rho_i(z, 0) \quad (36)$$

therefore equation (31) becomes

$$s\tilde{\rho}_i(z, s) - D_i \frac{\partial^2}{\partial z^2} \tilde{\rho}_i(z, s) = \rho_i(z, 0) \quad (37)$$

The solution which satisfies the boundary condition equation (32) is

$$\tilde{\rho}_i(z, s) = \tilde{B}(s) e^{-z\sqrt{s/D_i}} + \rho_i/s \quad (38)$$

From here we get for the boundary condition Eq.(33), the mass conservation condition at the electrode wall,

$$\frac{\partial}{\partial z} \tilde{\rho}_i(z, s) = -\sqrt{s/D_i} [\tilde{\rho}_i(z, s) - \rho_i/s] \quad z = 0 \quad (39)$$

and

$$\tilde{\rho}_i(0, s) = \rho_i/s - \frac{m}{\sqrt{sD_i}} \frac{\partial \theta_i}{\partial t} \quad (40)$$

The inverse Laplace transform of this equation yields

$$\gamma_i(t) = 1 - \frac{m}{\rho_i \sqrt{\pi D_i}} \int_0^t dt_1 \frac{1}{\sqrt{t-t_1}} \frac{\partial \theta_i}{\partial t_1} \quad (41)$$

where $\gamma_i(t)$ is defined in Eq.(27). This is the well known result for diffusion [19].

For linear potential scanning we can write, for $\psi = \psi_0 + vt$

$$\gamma_i(\psi) = 1 - \frac{m\sqrt{v}}{\rho_i \sqrt{\pi D_i}} \int_{\psi_0}^{\psi} d\psi_1 \frac{1}{\sqrt{\psi_0 - \psi_1}} \frac{\partial \theta_i(\psi - \psi_1)}{\partial \psi_1} \quad (42)$$

For slow scanning rates, again, we may use the approximation

$$\theta_i = \theta_i^\infty$$

so that

$$\gamma_i(\psi) \simeq 1 - \frac{m\sqrt{v}}{\rho_i\sqrt{\pi D_i}} \int_{\psi_0}^{\psi} d\psi_1 \frac{1}{\sqrt{\psi_0 - \psi_1}} \frac{\partial \theta_i^\infty(\psi - \psi_1)}{\partial \psi_1} \quad (43)$$

4 THE CASE OF CU UPD ON GOLD

A case of particular interest is the underpotentia¹ deposition (UPD) of Cu onto Au(111) in the presence of sulphuric acid. As is known [22, 23] the voltammogram shows two distinct peaks, which do not appear in the other faces of gold, the (110) or (100) face, or when another anion, such as ClO_4^- is used. The observation is that this splitting of the copper deposition is specifically tied to the presence of HSO_4^- ions. The observation of strong chemical binding of the deposited copper to oxygen [24], strongly suggests that the bisulphate ion is chemisorbed to the substrate. For these reasons a model was suggested in which the bisulphate formed a $\sqrt{3} \times \sqrt{3}$ template (see Figure 2)[12]. This template leaves a honeycomb lattice of adsorption sites for the copper (Figure 3), which implies that the first peak of the voltammogram corresponds to the filling of 2/3 of the original adsorption sites of the Au(111) surface. The second peak is due to the replacement of the bisulphate by copper, which implies the filling of the remaining 1/3 of the available sites (Figure 4). This model is in accordance with the experiments of Itaya [25] and Kolb [22].

The system undergoes three phase transitions [13, 14, 20]:

1. An order-disorder second order hard hexagon phase transition, due to the desorption of the bisulphate ions. In the presence of copper, the bisulphate is readsorbed, and the honeycomb template is reconstructed. This corresponds to the broad foot of the first peak.
2. A first order transition on the honeycomb lattice (Figure 3), corresponding to the first peak of the voltammogram.

3. A first order transition on the $\sqrt{3} \times \sqrt{3}$ triangular lattice, caused by the displacement of the bisulphate by copper.

The dynamics of this system was recently reexamined [26, 27]. There are two ions that participate in the transport of charge:

- The bisulphate, that carries a negative charge which it keeps when adsorbed onto the surface. Therefore, it will contribute only to the capacitive current density j_C . The other contribution to j_C is from the diffuse layer.
- The copper, which is adsorbed and discharged to some extent. It's electrovalence will change from ν_i in the bulk phase to ζ_i at the electrode interface. Furthermore, ζ_i should be a function of the potential ψ

Therefore, the total current density is (for a recent discussion see, for example the work of De Levie [21] and Lantelme [11])

$$j_T = j_C + j_F \quad (44)$$

where j_T is the total current density, j_C is the capacitive contribution and j_F is the Faradaic contribution. If we neglect double layer effects, then the capacitive current is due to the bisulphate, and the faradaic current almost exclusively to the discharge of the copper ions. Then

$$j_C = (1/A) \left[C_i + \psi \frac{dC_i}{d\psi} \right] \frac{d\psi}{dt} \quad (45)$$

gives the current due to the discharge of the capacitor as well as its change in capacitance.

The current associated with the cation (in this case the copper) can be written as

$$j_F = (eM/A) \left[\theta_i \frac{d\zeta_i}{d\psi} + \zeta_i \frac{d\theta_i}{d\psi} \right] \frac{d\psi}{dt} \quad (46)$$

where M is the number of adsorption sites per area A , e is the elementary charge, ζ_i is the electrovalence, and ψ the potential.

The charge of the adsorbate will change with the applied potential because the electron density at the surface is changing. Intuitively we take the exponential form

$$\zeta_1(t) = e^{\omega_c(\psi - \psi_1^{Re})}, \quad (47)$$

where ω_c and ψ_1^{Re} are adjustable parameters, responsible for the broadening of the baseline of the voltammogram. In our model it represents the change in charge with potential, which we believe is a monotonic and smooth function of the potential.

We consider only the copper current in the calculations. The bisulphate current contributes only to the broad foot of the first peak of the voltammogram, and will be discussed in future work. We have solved equations (17) and (42) numerically, and we fitted the three regions of Kolb's voltammogram to our theory. A plausible explanation for the smaller diffusion constants of the second peak is that there are very different double layer barriers for the ions in this case. We hope to come back to this point in the future.

Based on the fact that for very sharp transitions the most important consideration is that condition Eq.(8) is satisfied, so that for the purposes of this discussion we choose the kinetic adsorption constant equations Eq.(4),(ref.[14]) to be of the form

$$K_a \rho_i|_p = K_a e^{(n_{Cu,p} - m_{Cu,p})\beta e[\zeta_{Cu,p}(\psi_{Cu,p} - \psi_{Cu,p}^{Re})]} \quad (48)$$

and the kinetic desorption constant

$$K_d \rho_i|_p = K_d e^{m_{Cu,p}\beta e[\zeta_{Cu,p}(\psi_{Cu,p} - \psi_{Cu,p}^{Re})]} \quad (49)$$

These forms will satisfy equation (6) with the simplified form of \mathcal{A} taken from equation (22). For each of the three regions, the foot ($p=1$), the first peak ($p=2$) and the second peak ($p=3$), we fit the voltammogram to a set of kinetic constants. For the broad foot of the first peak the effect of diffusion has been neglected, and therefore a very large value of the diffusion constant is displayed.

Figures 5 and 6 show the result of our calculations, and reflect rather good agreement, except for the region of the broad foot, where the bisulphate current is missing.

In summary, our extension to the dynamic regime provides a way to calculate overall kinetic parameters from the shifts of the peaks in the voltammograms of processes with phase transitions.

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FIGURE CAPTIONS

FIGURE 1

Shifts of the voltammogram peak for a single peak. The width of the peak is proportional to $4/n$ for large n .

FIGURE 2

Geometry of the ordered adlayer with $1/3$ bisulphate.

FIGURE 3

Geometry of the adlayer with $1/3$ bisulphate and $2/3$ of copper. The copper ring holds the bisulphate structure, but the top of the bisulphate is still higher than the copper.

FIGURE 4

Geometry of the adlayer when the $1/3$ bisulphate has been replaced by copper. The bisulphate however is still adsorbed on top of the copper.

FIGURE 5

Copper adsorption isotherm showing the ordered phase for high voltage, the disordered phase between $0.22V$ and $0.45V$, and the ordered region between $0.22V$ and the bulk deposition.

FIGURE 6

Comparison of the theory to Kolb's voltammogram [23], for $0.1M$ H_2SO_4 , $10^{-3}M$ $CuSO_4$ and a scanning rate of $1mV/s$. The theory includes only the copper contribution. The parameters are:

Foot(1): $\mathcal{K}_a = 1.0, \mathcal{K}_d = 1.0, D = 0.9$

Peak 1(2): $\mathcal{K}_a = 0.23, \mathcal{K}_d = 0.11, D = 1.0 \times 10^{-5}, n_1 = 9, m_1 = 5$

Peak 2(3): $\mathcal{K}_a = 0.003, \mathcal{K}_d = 0.05, D = 1.0 \times 10^{-6}, n_1 = 6, m_1 = 4$

Figure 1

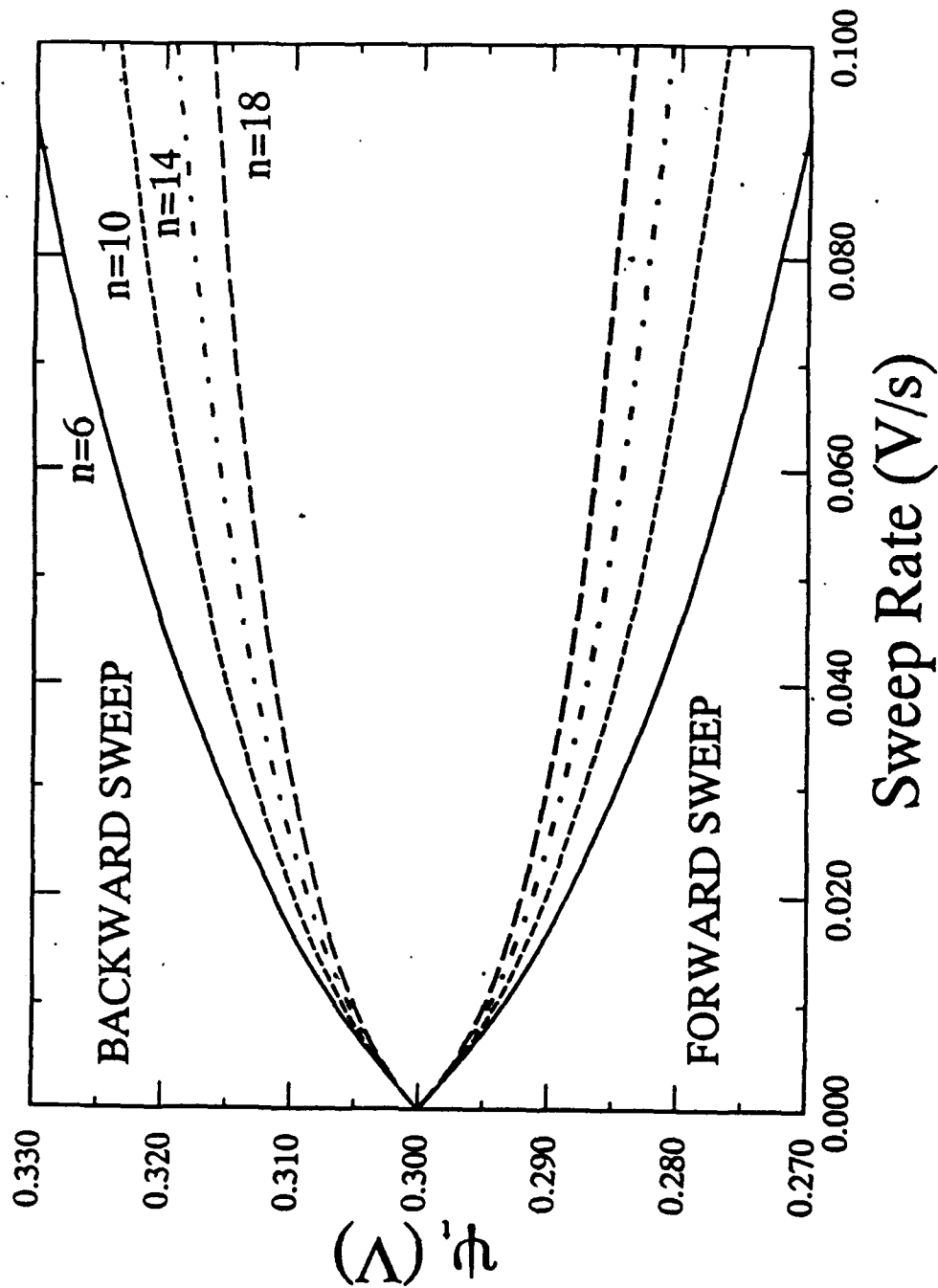


Figure 2

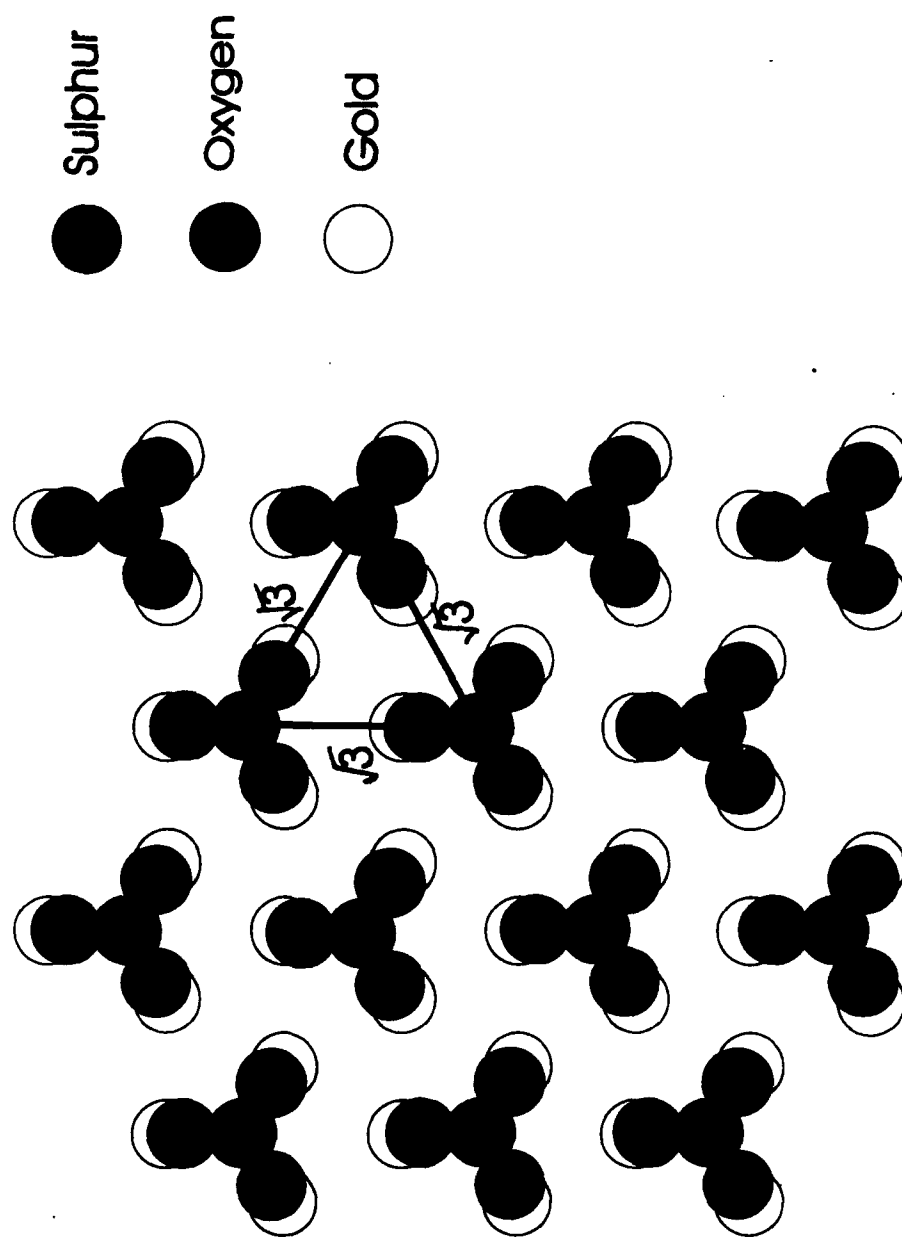


Figure 3

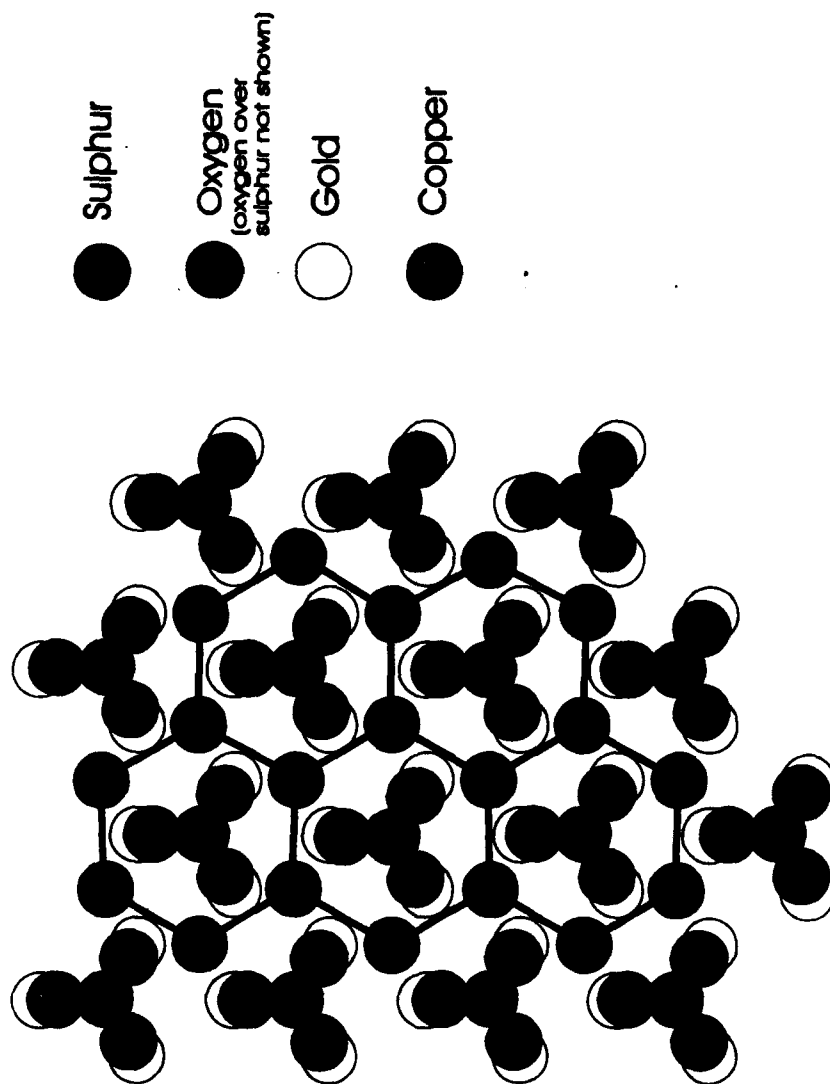


Figure 4

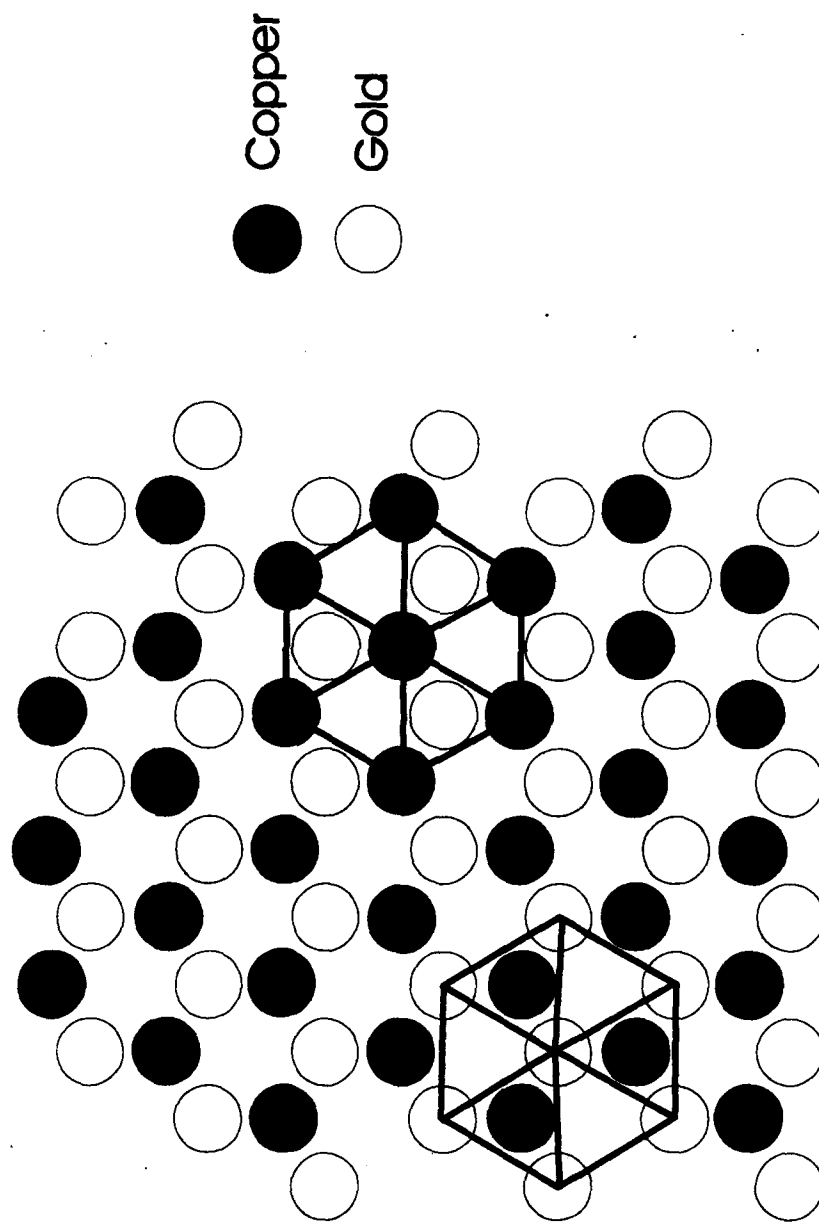


Figure 5

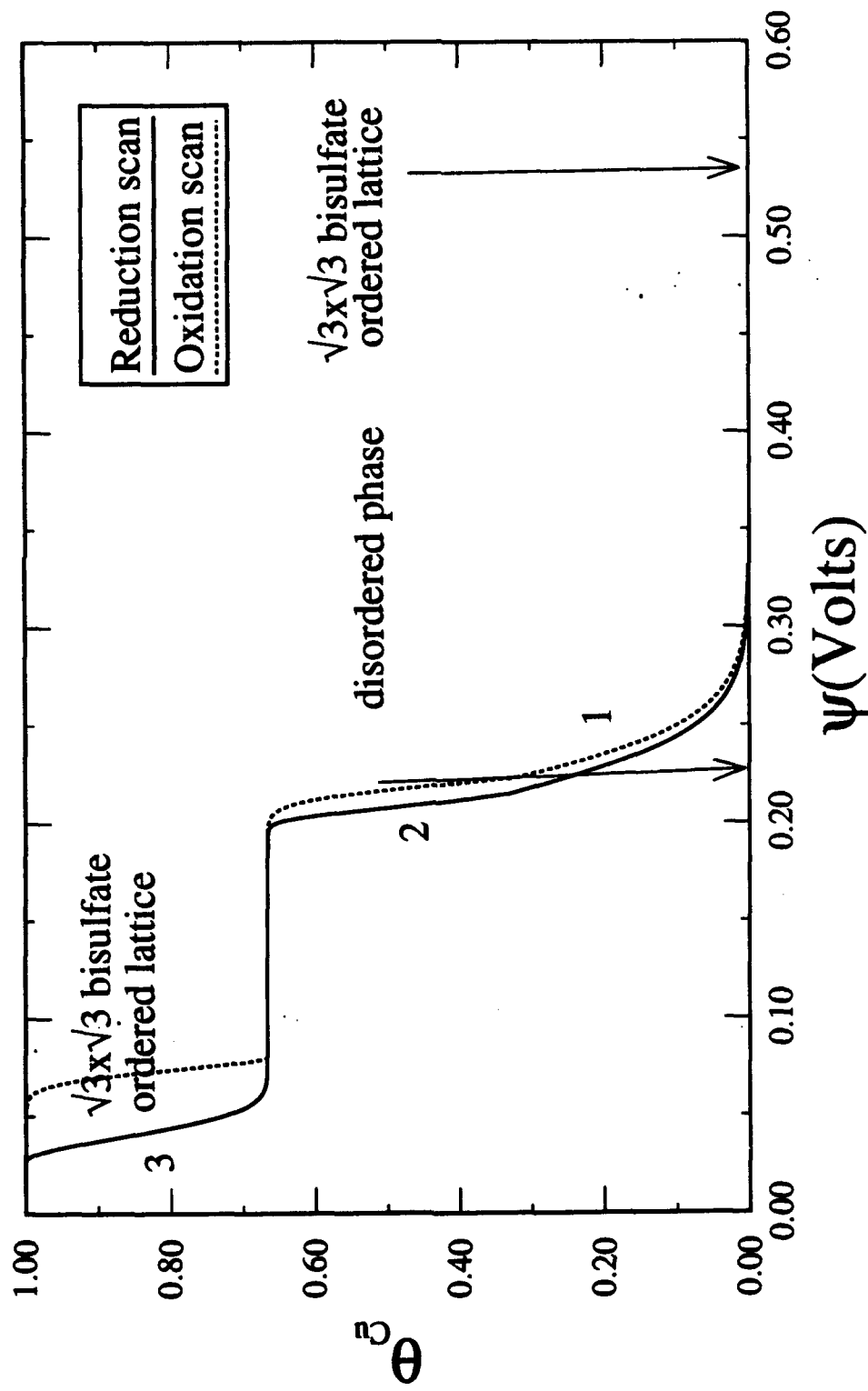


Figure 6

